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Reductive Cyclisation of 2-Azidocinnamates to 2-Substituted Quinolines

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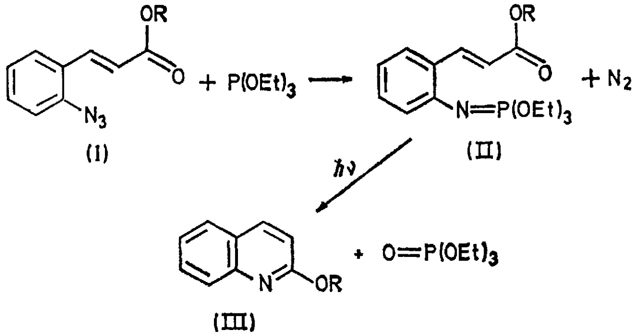
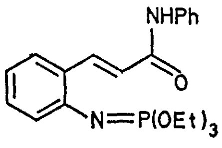
Summary Triethyl phosphite reacts with 2-azidocinnamates to give phosphorimidate intermediates, which can be cyclised photolytically to 2-substituted quinolines.

Reductive cyclisations of nitro- and nitroso-derivatives using trivalent phosphorus compounds leading to five-membered heterocycles are well known.[1] Cyclisation to six-membered rings on the other hand is comparatively rare, often requiring prior formation of a five-membered ring followed by rearrangement.[2]

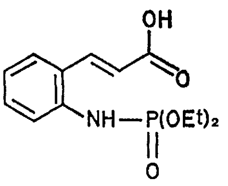


Scheme

We report here a simple reaction leading directly to the quinoline ring system, involving the reaction of triethyl phosphite with 2-azidocinnamates (Scheme). Thus, phenyl 2-azidocinnamate (I; R = Ph) (0·265 g), when warmed (50°; 10 min) with triethyl phosphite (0·183 g) in cyclohexane (2 ml), gave the expected phosphorimidate intermediate (II; R = Ph) with the evolution of nitrogen. The identity of the intermediate was confirmed by mass spectrometry. Irradiation of (II; R = Ph), in cyclohexane (300 ml) with 365 nm u.v. light for 30 min in a falling film apparatus,[3] caused a marked reduction in the fluorescence of the solution, and evaporation followed by recrystallisation from light petroleum (b.p. 40—60°) gave pale yellow flakes, m.p. 62—64° of 2-phenoxyquinoline (III; R = Ph) (95% crude). Similar reactions occur in high yield (>75%) with compounds (I; R = H, Me, or C_6H_{11}), but the phosphorimidate (IV) formed from 2-azidocinnamanilide failed to cyclise.



(IV)



(V)

The proposed mechanism is similar to that for the cyclisation of 2-azidophenyl benzoate to 2-phenylbenzoxazole,[4] but whereas in the latter case the phosphorimidate intermediate cyclised spontaneously at room temperature, in the cinnamate reaction the corresponding intermediate (II; R = Ph) withstood heating for 12 h at 110° in decalin solution. The intermediate (II; R = H) proved less stable thermally. However, the product of thermal decomposition was not carbostyril (III; R = H) but a crystalline product, m.p. 208—212°, which gave analytical data consistent with the formulation (V). We suggest that photolysis isomerises intermediates (II) from the *trans*- to the *cis*-form, thus bringing the reacting ester carbonyl and phosphorimidate groups into close enough proximity for reaction to occur. Cyclisation takes place with extreme ease since its quantum yield was found to be high [0·90 ± 0·10 for (II; R = Ph)].

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[2] J. I. G. Cadogan and S. Kulik, *J. Chem. Soc.* (*C*), 1971, 2621, and references therein.
[3] S. D. Cohen, M. V. Mijović, G. A. Newman, and E. Pitts, *Chem. and Ind.*, 1967, 1079.
[4] L. J. Leyshon and D. G. Saunders, *Chem. Comm.*, 1971, 1608.